



Short communication

A new concept of combined NH_3 -CO-SCR system for efficient NO reduction in excess oxygenAsima Sultana^{*}, Masaaki Haneda, Hideaki Hamada

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ABSTRACT

A new concept of a novel “dual bed” configuration of NH_3 and CO-SCR catalytic system (NH_3 -CO-SCR), comprising Cu/Beta as top catalyst bed for NH_3 -SCR and $\text{WO}_3/\text{Ir}/\text{SiO}_2$ as bottom catalyst bed for CO-SCR, is described in this article. The combined catalytic system provides high NO reduction efficiency, in a broad temperature range (160–600 °C). The NO conversion over the combined catalytic system reached up to 98% between 280 and 320 °C, as compared to the system using only Cu/Beta or $\text{WO}_3/\text{Ir}/\text{SiO}_2$ with sole NH_3 or CO as reductant. Furthermore, the combined catalytic system shows high NO reduction efficiency even in the presence of lower concentrations of NH_3 and CO. Thus, the potential advantage of this combined system is that it can effectively reduce NO during situations when NH_3 and CO concentration is expected to fluctuate in real driving conditions which could potentially lead to NH_3 and CO slip issues.

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1. Introduction

Worldwide environmental regulations regarding NO_x emissions from diesel engines have become significantly more stringent leading to innovative applications of new technologies to resolve the problem. As a potent technology, the selective catalytic reduction (SCR) of NO has been studied intensively using various reductants [1–6]. A broad temperature range of high activity is a prerequisite for a practical catalyst. Recently, Ir/WO_3 , Ir/SiO_2 and $\text{Ir}/\text{WO}_3/\text{SiO}_2$ were found to be highly active catalysts for NO reduction with CO (CO-SCR) [7–11]. However, these catalysts are active only in a narrow temperature range (260–400 °C). With an appropriate catalyst urea or NH_3 can function as a very good selective NO_x reductant in a broad temperature range [12]. However, the NO reduction activity depends on the inlet NH_3 concentration, too little ammonia leads to low NO conversion and too much ammonia can result in ammonia slip. Thus, it is important not only to reduce inlet NH_3 concentration to avoid ammonia slip, but also to achieve high NO conversion in the presence of reduced NH_3 concentration. Moreover, the emissions from a motor vehicle vary under different driving conditions. Thus, an ideal catalyst should work under these varying exhaust gas concentrations.

One of the strategies to solve the above problems and achieve greater NO_x reduction efficiency is selective reduction of NO using mixed reductants, thereby reducing the inlet NH_3 concentration. Recently, a few attempts have been made to improve the NO_x reduction efficiency by using mixed reductants [13]. However, the so far developed catalysts or catalytic systems used for SCR show inefficiency in complete NO_x removal in a broad temperature window. In the present study, we are proposing and demonstrating a new concept of dual reductant (NH_3 + CO), dual catalyst bed (Cu/Beta + $\text{WO}_3/\text{Ir}/\text{SiO}_2$) SCR system, which shows high NO reduction efficiency in a broad temperature window even in presence of lower CO and NH_3 concentrations.

2. Experimental

0.5 wt% Ir/SiO_2 was prepared by impregnation of SiO_2 support (Fuji Silysia Chemicals, Cariat G-10, S.A. = 300 $\text{m}^2 \text{g}^{-1}$) with aqueous solution of $\text{Ir}(\text{NH}_3)_6(\text{OH})_3$. 10 wt% $\text{WO}_3/\text{Ir}/\text{SiO}_2$ was prepared by addition of $(\text{NH}_4)_{10}\text{W}_{12}\text{O}_{41} \cdot 5\text{H}_2\text{O}$, dissolved in citric acid solution to Ir/SiO_2 . Cu/Beta (Tosoh Corporation, HSZ-930, $\text{SiO}_2/\text{Al}_2\text{O}_3 = 27$, S.A. = 630 $\text{m}^2 \text{g}^{-1}$) was prepared by ion-exchange using $\text{Cu}(\text{NO}_3)_2$ solution. The prepared samples were dried at 110 °C overnight, followed by calcination at 600 °C for 6 h in air. Prior to reaction, the catalysts were pretreated in He flow at 600 °C for 1 h and the catalytic activity was measured using a fixed bed flow reactor. The dual bed catalytic system consisted of, Cu/Beta as top catalyst bed, which is active for NO_x reduction with NH_3 and $\text{WO}_3/\text{Ir}/\text{SiO}_2$ as bottom catalyst bed, which is active for NO_x reduction with

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CO. The two catalytic beds were separated by quartz wool. The standard reaction gas mixture consisted of 500 ppm NO, 3000 ppm CO, 500 ppm NH₃, 5% O₂, 6% H₂O, 1 ppm SO₂ and He as balance gas was fed through a catalyst (40 mg) at a rate of 90 cm³ min⁻¹ (SV = ca. 75,000 h⁻¹). Dual bed system, consisted of 40 + 40 mg (SV = ca. 75,000 h⁻¹ at each catalyst or overall 37,500 h⁻¹) of Cu/Beta + WO₃/Ir/SiO₂ catalysts. In a few of the experiments the NO, O₂, SO₂ and H₂O concentrations were kept the same, and only CO and NH₃ concentrations were varied from 3000 to 1000 ppm and 500 to 200 ppm respectively. The reactants and the products were analyzed by gas chromatography and a chemiluminescence analyzer.

3. Results and discussions

The combined NH₃-CO-SCR catalytic system is shown schematically in Fig. 1. In the combined catalytic system, it is expected that NO would preferentially react with NH₃ over the top Cu/Beta catalyst bed and with CO on the bottom WO₃/Ir/SiO₂ catalyst bed. It is necessary that the top catalyst bed should be inactive towards the oxidation of CO, otherwise CO will not be available for NO reduction over the bottom WO₃/Ir/SiO₂ catalyst bed. The unreacted CO and NO from the top catalyst bed, react over the bottom catalyst bed (WO₃/Ir/SiO₂), which is active for selective reduction of NO with CO. The combined catalytic system is therefore expected to show better NO reduction activity with mixed, NH₃ and CO, reductants than the single catalytic bed system having only Cu/Beta or WO₃/Ir/SiO₂ catalyst. More particularly, combined catalytic system is expected to show improvement in NO reduction activity at low temperature due to combined activity of Cu/Beta + WO₃/Ir/SiO₂ catalysts even in the presence of lower concentrations of the reductants which is difficult to obtain with single Cu/Beta or WO₃/Ir/SiO₂ catalytic system. Thus, in the present study, we explored the possibility of potential improvement of NO reduction activity using a combined NH₃-CO-SCR catalytic system in a dual bed configuration taking advantage of the desirable characteristics of each system.

The NO reduction activities of WO₃/Ir/SiO₂ with CO, Cu/Beta with NH₃ and Cu/Beta + WO₃/Ir/SiO₂ with NH₃ + CO as reductants at different temperatures are shown in Fig. 2. WO₃/Ir/SiO₂ catalyst exhibits high NO_x reduction activity with CO, but in a narrow temperature window of 260–400 °C with a maximum conversion of 70% at 300 °C. Reduction of NO over single bed WO₃/Ir/SiO₂ with NH₃ + CO as mixed reductants, showed slightly higher

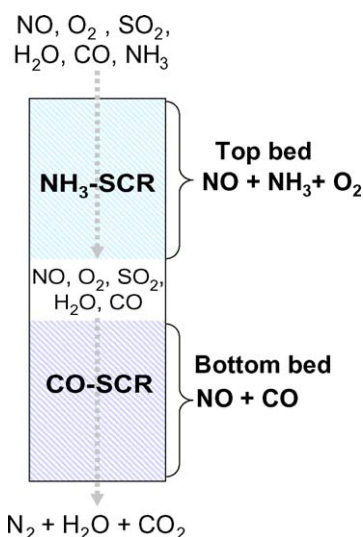


Fig. 1. NH₃-CO-SCR over combined Cu/Beta + WO₃/Ir/SiO₂ catalytic system.

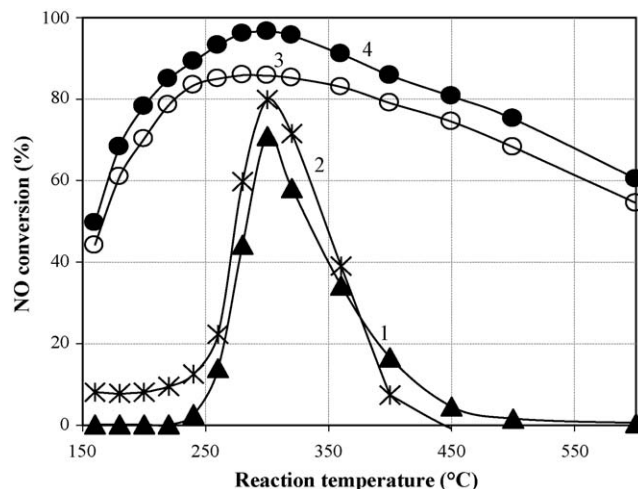


Fig. 2. NO conversion over (1) WO₃/Ir/SiO₂ with CO (3000 ppm), (2) WO₃/Ir/SiO₂ with NH₃ + CO (500 + 3000 ppm), (3) Cu/Beta with NH₃ + CO (500 + 3000 ppm) and (4) Cu/Beta + WO₃/Ir/SiO₂ with NH₃ + CO (500 + 3000 ppm). Reaction conditions: 500 ppm NO, 5% O₂, 6% H₂O, 1 ppm SO₂, NH₃ and CO (SV = single catalyst bed—ca. 75,000 h⁻¹ and dual catalyst bed—ca. 37,500 h⁻¹ overall or 75,000 h⁻¹ at each catalyst bed).

activity in the lower temperature region ($T < 360$ °C). However, the high temperature activity ($T > 400$ °C) was found to decrease due to oxidation of ammonia by oxygen. On the other hand, among the different Cu/zeolite catalysts tested, Cu/Beta catalyst showed the highest NO reduction activity in the presence of equimolar amount of NO and NH₃ in the entire range of reaction temperature (160–600 °C) studied, with maximum NO conversion reaching up to 88%. There was almost no change in NO reduction activity of Cu/Beta with NH₃ in presence of CO. Moreover, Cu/Beta does not show any CO oxidation activity below 350 °C. This result suggests that Cu/Beta is active for NO reduction only with NH₃ and not with CO.

The combined catalytic system, with Cu/Beta as top catalyst bed and WO₃/Ir/SiO₂ as bottom catalyst bed shows high NO reduction efficiency (>90%). The high temperature activity at $T > 400$ °C over Cu/Beta + WO₃/Ir/SiO₂ combined catalytic system is expected to arise from NH₃-SCR over Cu/Beta. Whereas, the low temperature activity, below 400 °C, is expected due to additive effect of NO conversion over Cu/Beta and WO₃/Ir/SiO₂ catalysts with NH₃ and CO respectively. All the catalysts tested showed high N₂ product selectivities. The N₂ product selectivities as a function of temperature for WO₃/Ir/SiO₂, Cu/Beta and Cu/Beta + WO₃/Ir/SiO₂ catalysts are shown in Fig. 3. Cu/Beta showed the higher N₂ (99%) product selectivity below 450 °C than WO₃/Ir/SiO₂ catalyst (95%). The dual bed catalytic system not only showed high NO conversion, but also maintained high N₂ (96%) product selectivity.

It is known that the extent of NO reduction activity depends on the type and concentration of the reductant. In NH₃-SCR, the concentration of NH₃ with respect to NO affects the degree of NO_x reduction as well as the NH₃ slip [14]. In a typical exhaust gas, the ammonia concentration could vary from a few ppm to several thousand ppm and its variation lead to ammonia slip issues and also significantly affects the downstream NH₃ conversion over NH₃ cleaning catalyst [15]. Therefore, the effectiveness of the dual bed catalytic system was also examined with different NH₃ concentrations (500–200 ppm), while keeping the CO concentration constant (3000 ppm). Fig. 4 shows the NO reduction activity of Cu/Beta + WO₃/Ir/SiO₂ dual bed catalytic system under varying concentrations of NH₃. The high temperature ($T > 400$ °C) NO

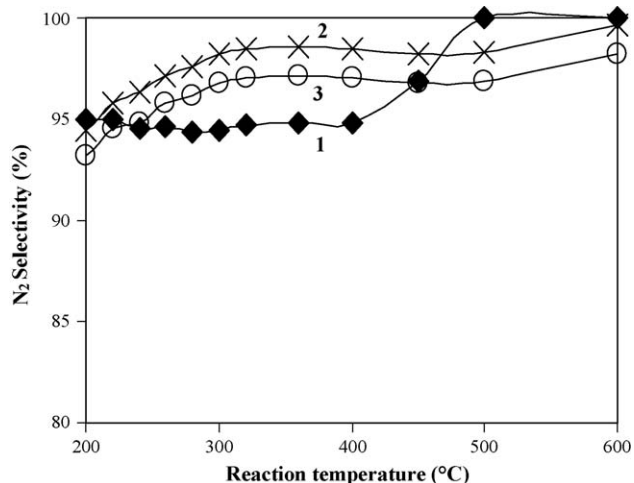


Fig. 3. N₂ selectivity of (1) WO₃/Ir/SiO₂, (2) Cu/Beta and (3) Cu/Beta + WO₃/Ir/SiO₂ catalysts as a function of temperature. Reaction conditions: 500 ppm NO, 5% O₂, 6% H₂O, 1 ppm SO₂ and 500 ppm NH₃, 3000 ppm CO or 500 + 3000 ppm NH₃ + CO (SV = single catalyst bed—ca. 75,000 h⁻¹ and dual catalyst bed—ca. 37,500 h⁻¹ overall or 75,000 h⁻¹ at each catalyst bed).

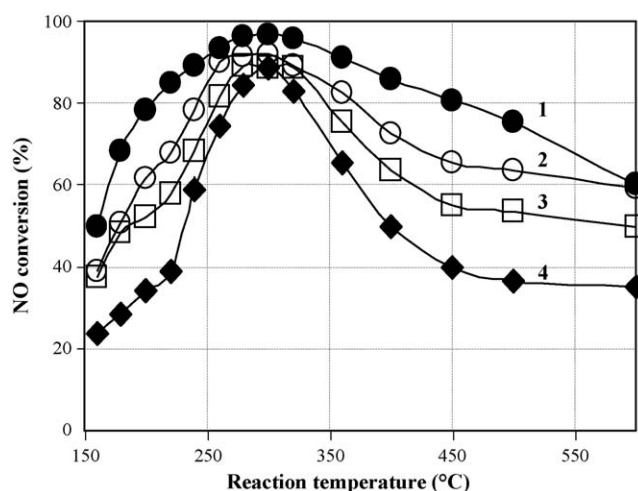


Fig. 4. Effect of varying NH₃ concentration on NO conversion over Cu/Beta + WO₃/Ir/SiO₂ dual bed catalyst. (1) 500 ppm, (2) 400 ppm, (3) 300 ppm and (4) 200 ppm. Reaction conditions: 500 ppm NO, 5% O₂, 6% H₂O, 1 ppm SO₂, 3000 ppm CO and 500–200 ppm NH₃ (SV = ca. 37,500 h⁻¹ overall or 75,000 h⁻¹ at each catalyst bed).

reduction activity of the dual bed catalytic system decreased with decrease in inlet NH₃ concentration, however, it showed high NO reduction activity >80% at 300 °C, even in the presence of low concentration of NH₃ (200 ppm) and CO (3000 ppm). On the other hand, the NO reduction activity of the single bed Cu/Beta catalyst showed decrease in NO reduction activity from 88 to 39% at 300 °C with decrease in NH₃ concentration from 500 to 200 ppm (Fig. 5). The NO reduction activity of WO₃/Ir/SiO₂ catalyst was also found to significantly decrease from 70 to 10% at 300 °C with decrease in CO concentration from 3000 to 1000 ppm (Fig. 6).

Taking into account the limits on catalyst amount due to cost, and limits on catalyst bed size due to engine back pressure intolerance, the efficiency of the dual bed catalytic system was also tested using the less amount (20 + 20 mg) of catalyst. A comparison of the catalytic activity of dual bed Cu/Beta + WO₃/Ir/SiO₂ catalytic system with NH₃ + CO and single bed Cu/Beta with NH₃ and WO₃/Ir/SiO₂ with CO at the same space velocity is shown in

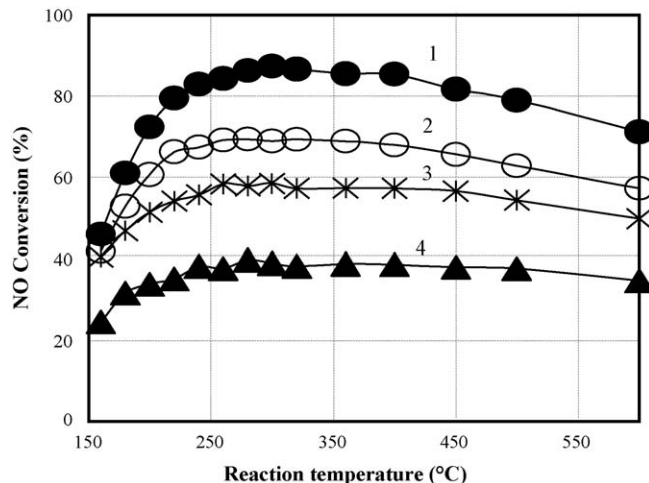


Fig. 5. Effect of NH₃ concentration on NO conversion over Cu/Beta catalyst. (1) 500 ppm, (2) 400 ppm, (3) 300 ppm and (4) 200 ppm. Reaction conditions: 500 ppm NO, 5% O₂, 6% H₂O, 1 ppm SO₂, 500–200 ppm NH₃ (SV = ca. 75,000 h⁻¹).

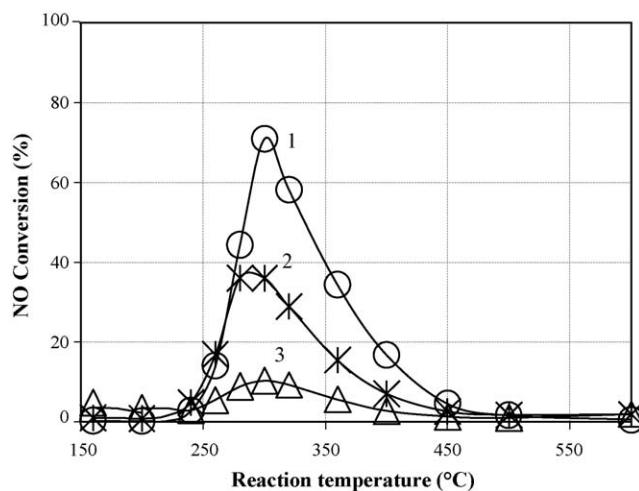


Fig. 6. Effect of CO concentration on NO conversion over WO₃/Ir/SiO₂ catalyst (1) 3000 ppm, (2) 2000 ppm and (3) 1000 ppm. Reaction conditions: 500 ppm NO, 5% O₂, 6% H₂O, 1 ppm SO₂ and 3000–1000 ppm CO (SV = ca. 75,000 h⁻¹).

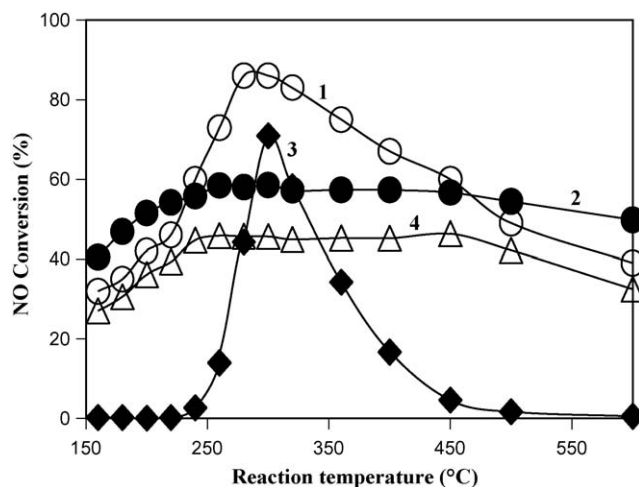


Fig. 7. Comparison of NO conversion over (1) Cu/Beta + WO₃/Ir/SiO₂ with NH₃ + CO (300 + 3000 ppm) (20 + 20 mg cat), (2) Cu/Beta with NH₃ (300 ppm) (40 mg cat) and (3) WO₃/Ir/SiO₂ with CO (3000 ppm) (40 mg cat), and catalyst at SV = ca. 75,000 h⁻¹ and (4) Cu/Beta with NH₃ (300 ppm) (20 mg cat) at SV = ca. 150,000 h⁻¹.

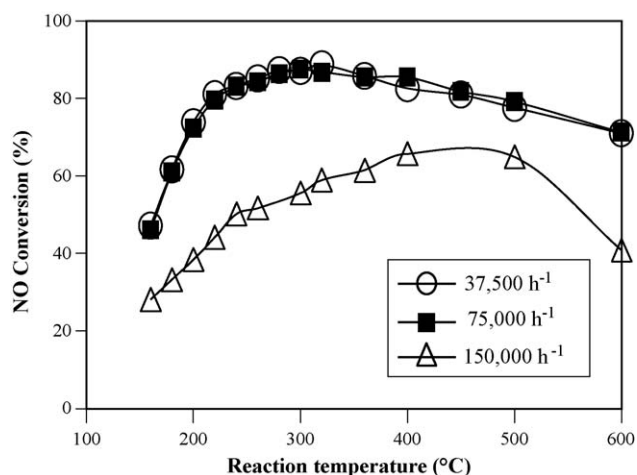


Fig. 8. Effect of space velocity on activity of single bed Cu/Beta for NH_3 -SCR. Reaction conditions: 500 ppm NO, 5% O_2 , 6% H_2O , 1 ppm SO_2 and 500 ppm NH_3 .

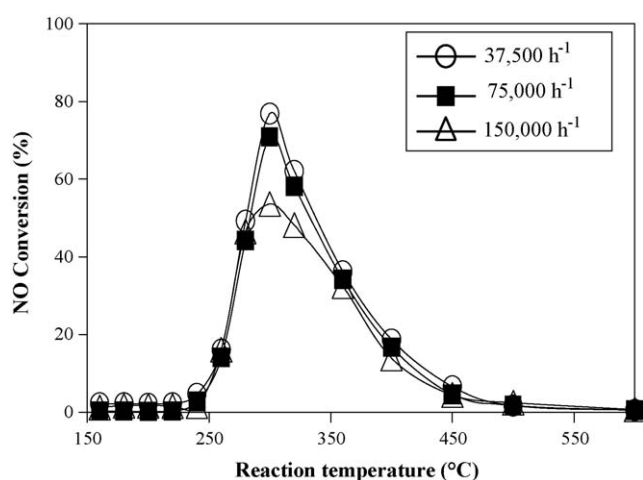


Fig. 9. Effect of space velocity on activity of single bed $\text{WO}_3/\text{Ir}/\text{SiO}_2$ for CO-SCR. Reaction conditions: 500 ppm NO, 5% O_2 , 6% H_2O , 1 ppm SO_2 and 3000 ppm CO.

Fig. 7. It is reasonable that the NO_x conversions decrease as the space velocity increases because the contact time of reactants on the catalyst surface decreases. However, it should be noted that the NO_x conversions are still quite high (>80% conversion between 260

and 300 °C) in case of dual bed $\text{Cu}/\text{Beta} + \text{WO}_3/\text{Ir}/\text{SiO}_2$ catalytic system with $\text{NH}_3 + \text{CO}$, even at a high space velocity ($75,000 \text{ h}^{-1}$) and lower amount of ammonia (300 ppm) compared to either of the individual catalyst. On the other hand, the activity of Cu/Beta catalyst (Fig. 8) with NH_3 and $\text{WO}_3/\text{Ir}/\text{SiO}_2$ (Fig. 9) catalyst with CO were found to be similar at 37,500 and $75,000 \text{ h}^{-1}$, but when the space velocity was increased from 75,000 to $150,000 \text{ h}^{-1}$, the decrease in activity became conspicuous.

Another consideration is the possibility to obtain the high overall NO reduction by varying the concentrations of both the NH_3 and CO reductants. Fig. 10A–C, shows the NO reduction activity of dual bed catalysts under different combinations of NH_3 and CO concentrations. Interestingly, the dual bed catalytic system even in the presence of a mixture of NH_3 (300 ppm)–CO (2000 ppm) (Fig. 10A-3), NH_3 (400 ppm)–CO (1000 ppm) (Fig. 10B-1) and NH_3 (200 ppm)–CO (2000 ppm) (Fig. 10 C-2) maintained superior NO reduction activity around 70% at 300 °C than either of the individual catalysts. The NO reduction activity over single bed Cu/Beta with 400, 300 and 200 ppm of NH_3 as sole reductant was 68, 56 and 38%, respectively. Similarly the NO conversions over single bed $\text{WO}_3/\text{Ir}/\text{SiO}_2$ catalyst with 2000 and 1000 ppm of CO were only 35 and 10% at 300 °C. The improvement in activity of the combined catalytic system is attributed to additive effect of conversion over Cu/Beta and $\text{WO}_3/\text{Ir}/\text{SiO}_2$ catalysts. This result reveals that the combined catalyst system would be more tolerant against fluctuations of the exhaust gas composition under different driving conditions. Another potential advantage is that the unreacted NH_3 downstream of Cu/Beta can be easily oxidized over $\text{WO}_3/\text{Ir}/\text{SiO}_2$ catalyst further reducing NH_3 slip associated problem. It was also found that, even the physical mixture of these two catalysts showed the same enhancement in NO reduction activity with a mixture of NH_3 and CO as reductants. Thus, the combined Cu/Beta and $\text{WO}_3/\text{Ir}/\text{SiO}_2$ catalytic system provides excellent NO reduction efficiency and could be a potential system for the utmost removal of NO from exhaust gas in a wide temperature window.

In conclusion, the combination of two catalysts ($\text{Cu}/\text{Beta} + \text{WO}_3/\text{Ir}/\text{SiO}_2$) in dual bed configuration for SCR of NO with NH_3 and CO (NH_3 -CO-SCR) exhibits better performance of selective catalytic reduction of NO than either of the individual catalytic systems. The potential advantage of this combined system is that it can effectively convert NO during situations when NH_3 and CO concentrations are expected to fluctuate in real driving conditions which could potentially lead to NH_3 slip issues. Ultimately, by combining the two SCR catalysts and two reductants, high NO_x emission control can be achieved compared with the NO_x reduction efficiency with a single bed and single reductant systems.

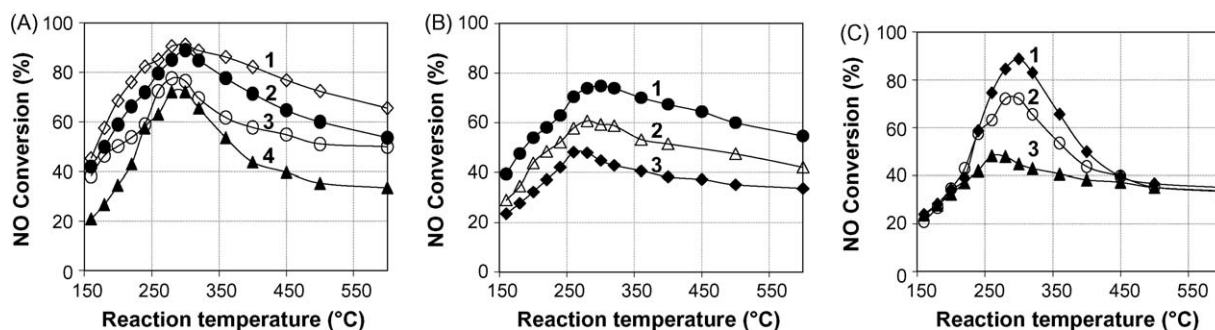


Fig. 10. Effect of varying $\text{NH}_3 + \text{CO}$ concentration on NO conversion over $\text{Cu}/\text{Beta} + \text{WO}_3/\text{Ir}/\text{SiO}_2$ dual bed catalysts. A-(1) 500 + 2000 ppm, (2) 400 + 2000 ppm, (3) 300 + 2000 ppm and (4) 200 + 2000 ppm, B-(1) 400 + 1000 ppm, (2) 300 + 1000 ppm and (3) 200 + 1000 ppm, C-(1) 200 + 3000, (2) 200 + 2000 and (3) 200 + 1000. Reaction conditions: 500 ppm NO, 5% O_2 , 6% H_2O , 1 ppm SO_2 , CO and NH_3 (SV = ca. $37,500 \text{ h}^{-1}$ overall or $75,000 \text{ h}^{-1}$ at each catalyst bed).

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